DESIGN, SYNTHESIS, AND APPLICATION OF NOVEL FLAME RETARDANTS DERIVED FROM BIOMASS

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Biomass represents an abundant and relatively low cost carbon resource that can be utilized to produce platform chemicals such as levulinic acid. Novel oligomeric flame retardants, the poly(MDP-PDCP-MA)s (PMPMs), were designed and synthesized using diphenolic acid as one of the raw materials, which is derived from levulinic acid. To change the molar ratio of reactants, a series of PMPM samples with different nitrogen contents were obtained and characterized by FTIR and solid-state ^{13}C NMR spectroscopy. The solubility test and thermogravimetric analysis (TGA) indicated a good solvent-resistant property and thermal stability. The flame retardancy and thermal behavior of ABS with 30% loading of different PMPM samples were investigated by limiting oxygen index test (LOI), TGA, and microscale combustion colorimeter (MCC). The results showed that PMPMs are effective charring agents that can increase the thermal stability and flame retardancy of ABS. Scanning electron microscopy (SEM) observations of the residue of ABS/PMPM blends indicated the compact charred layer formed was responsible for improving the thermal stability and char yield of ABS with low nitrogen content in PMPM-1 flame retardant.

Keywords: Diphenolic acid; Flame retardant; Synthesis; Biomass; Acrylonitrile butadiene styrene

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INTRODUCTION

Biomass resources are residues after crop or wood harvest in agriculture and forest industries that can be transformed into energy or forage. With increasing consumption of conventional energy, diminishing supply of fossil energy, environmental destruction, and climate change, efficient exploitation and more effective utilization of biomass resources have attracted attention all around the world (Yang *et al.* 2011; Cai *et al.* 2008). This necessity to extend the use of biomass as a sustainable resource for energy and as a chemical feedstock has triggered action plans in almost every industrial country or region of the world (Mahro and Timm 2007).

Currently, the development of ecologically friendly polymers and intumescent flame retardants (IFRs) based on phosphorus-nitrogen-containing compounds has received much attention (Lee *et al.* 2003). However, the raw materials of IFRs are almost entirely derived from the petrochemical industry, which are nonrenewable. If they could be replaced in part by chemicals from biomass resources, this would be a novel approach for the sustainable development of IFRs.

The National Renewable Energy Laboratory (Denver, USA) identified levulinic acid as one of a number of key sugar-derived platform chemicals that can be produced from lignocellulosic sources through acid-catalyzed dehydration and hydrolysis of hexose sugars (Bozell and Petersen 2010; Werpy and Petersen 2004; Rackemann and Doherty 2011). As one of the derivatives from levulinic acid, diphenolic acid (DPA, with the chemical name of 4,4-bis-(4'-hydroxyphenyl) pentanoic acid) has been deemed a new monomer in the preparation of reactive aromatic polyesters and polycarbonates due to its multifunctional groups (Wang and Nakamura 1995; Zhang and Moore 2002; Zhang and Moore 2003). However, little attention has been paid to their potential use as flame retardants. In previous research (Chen *et al.* 2011), poly(DPA-PDCP) (PDP) was obtained through simple interfacial polycondensation between DPA and phenyl dichlorophosphate (PDCP). When poly(DPA-PDCP) was introduced into ABS as a flame retardant, it acted as a charring agent to increase the char yield of the blends. However, since there is an active carboxyl in PDP, crosslinking may occur in the polymer (Moore and Tannahill 2001) and dehydration of carboxyls to form carbon dioxide can take place within the temperature range of 200 to 280 °C, such that bonds are already broken before the phosphorus-carbonaceous material is formed. That is to say, inert gas is released too early to expand the polymer, and it becomes difficult to form an effective swollen layer to hamper the diffusion of heat and combustible gas. At the same time, the dehydration temperature of poly(DPA-PDCP) began from 200°C, which is near the processing temperature of ABS. There is a risk that degradation of PDP may take place during processing. Therefore, hydrolytic instability of PDP may limit the effectiveness of its flame retardancy and its application.

Results of a series of experiments demonstrated the roles of melamine (Markarian 2005; Braun and Schartel 2005; Mukherjee 2001). Melamine may facilitate the phosphorylation and is believed to serve as a blowing agent in the intumescent formulation as part of the volatiles emitted during pyrolysis, which include water, CO, CO_2, ammonia, and hydrocarbons, all serving to foam the char (Lewin 1999). At the same time, its amino groups are easier to carry out esterification with carboxyl groups or transesterification with ester groups. Therefore, melamine was introduced into the structure of PDP to produce a series of novel oligomeric IFRs, *i.e.* poly(MDP-PDCP-MA)s (PMPMs), as described in this paper. Through diminishing the number of active carboxyl groups in the molecule, the structures of the flame retardants was optimized to improve their thermal stability. The structure of the novel IFRs was characterized by FTIR and solid-state ^{13}C NMR. The effects of PMPMs on the flame retardancy and thermal decomposition behavior of ABS were studied by limiting oxygen index test (LOI), thermogravimetric analysis (TGA), and microscale combustion colorimeter (MCC). The morphology of the char layer was also investigated so as to correlate the molecular structure of IFRs with the flame retardant behavior of the system.

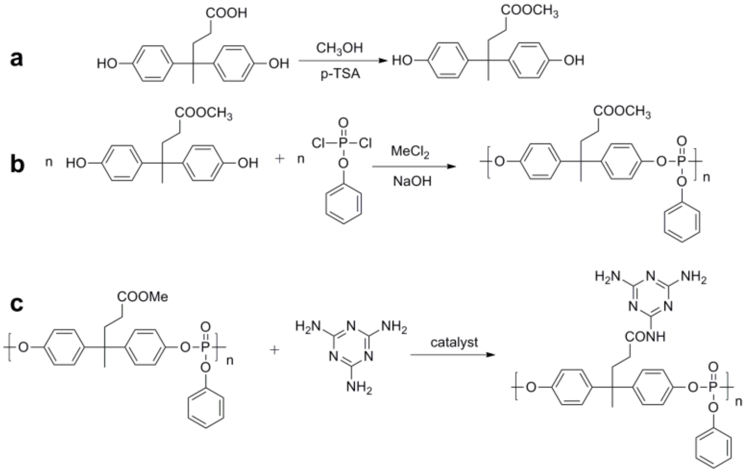
EXPERIMENTAL

Materials

Acrylonitrile-butadiene-styrene (ABS) copolymer (GP22), with a melt flow index of 1.6 g/10 min and a density of 1.04 g/cm^3, was obtained commercially from BASF Industries, Korea. Diphenolic acid (DPA, 98%) was provided by Hebei Yanuo Chemical Industry Co., Ltd. Phenyl dichlorophosphate (99%, PDCP) was provided by Jingyan Chemicals Co., Ltd. (Shanghai, China). Anhydrous methanol (CH_3OH), p-toluenesulfonic acid (PTSA), dichloromethane (CH_2Cl_2), sodium hydroxide (NaOH), tetrabutylammonium chloride (TBAC), melamine (MA), and zinc acetate ($Zn(OOCCH_3)_2{\bullet}2H_2O$) were provided by Sinopharm Chemical Reagent Co., Ltd. All chemical reagents were A. R. grade and were used without further purification.

Synthesis of Methyl Diphenolate (MDP)

The intermediate, methyl diphenolate (MDP, with the chemical name of methyl 4,4'-bis(4-hydroxyphenyl)valerate), was synthesized according to the literature (Moore and Tannahill 2001). A mixture of DPA (5.726 g, 20 mmol) and PTSA (0.344 g, 2 mmol) in 200 mL from methanol was added in a 250 mL one-neck flask equipped with a reflux condenser. The solution was heated and refluxed for 8 h. White solid product was obtained after the solvent was removed by rotary evaporation. The product was crystallized in CH_3OH/H_2O and dried in a vacuum oven overnight at 60 °C (yield 85%). The synthesis route is illustrated in Scheme 1(a).



Scheme 1. Synthesis of PMP and PMPM-1

Synthesis of Poly(MDP-PDCP) (PMP)

A 100 mL, three neck, round bottom flask was equipped with mechanical stirring. A typical interfacial polycondensation process was as follows (Sun *et al.* 1997): MDP (5 mmol, 1.005 g), TBAC (0.06 g), and NaOH (10 mmol, 0.4 g) were added into 10 mL water. Then, 10 mL dichloromethane solution containing 5 mmol of PDCP was quickly added to the resulting aqueous solution during vigorous stirring. After reaction at 25 °C for 2 to 3 h, PMP was obtained. The product was washed with deionized water and anhydrous ethanol and dried at 80 °C in a vacuum oven to constant weight (70% yield). The synthesis route is illustrated in Scheme 1(b).

Synthesis of Poly(MDP-PDCP-MA) (PMPM)

A mixture of PMP, melamine (MA), anhydrous zinc acetate (dried in vacuum at 80 °C to constant weight before experiment), and deionized water were added into a one-neck flask equipped with a reflux condenser. After the mixture was stirred for 6 h at 100 °C, the yellow solid PMPM was obtained. The product was washed with hot water several times until residue MA was totally removed, then dried at 90 °C in a vacuum oven overnight (65% yield). The synthesis route is illustrated in Scheme 1(c). In a similar procedure (the reaction mole ratio of PMP and MA was changed), a series of PMPMs were obtained with various phosphorus-nitrogen ratios. The content of the elements in different PMPMs was analyzed by an elemental analyzer and the results are listed in Table 1.

Table 1. PMPM Flame Retardants Containing Different Nitrogen Contents

PMPM	n_{PMP}/n_{MA}	**Anal. Calc. Molar Ratio for P/N**	**Found N% (Elemental Analysis)**
PMPM-1	4:1	2:3	1.8
PMPM-2	2:1	1:3	2.4
PMPM-3	1:1	1:6	5.2
PMPM-4	1:2	1:12	7.0

Preparation of Flame-Retardant ABS Blends

Flame-retardant ABS blends with 30% loading of different PMPMs were prepared via melt compounding at 180 °C in a ThermoHaake rheomixer with a rotor speed of 60 rpm for a mixing time of 8 min for each sample. Then, the prepared blends were transferred to a mold and preheated for 6 min at 180 °C and pressed at 15 MPa for 10 min, followed by pressing at room temperature while maintaining the same pressure for another 5 min. The sample sheets were stored for further tests.

Methods

Infrared spectra (IR) were recorded on a Vector-22 FTIR spectrometer using KBr pellets. A Chemagnetics CMX-400 with a magic-angle spinning double resonance probe was used for data collection in solid-state ^{13}C NMR spectra operating at 75.39 MHz. The contact time was 1.5 ms and the repetition time was 3 s. The $\pi/2$ pulse width for protons was 4 μs. The samples were placed in a cylindrical rotor and spun at maximum 8.0 kHz. Chemical shifts were referenced using hexamethylbenzene as an external standard. Elemental analyses were carried out using a ThermoFinnigan analyzer (Flash EA 1112).

TG analysis was performed on a TA STD Q600 thermal analyzer at a heating rate of 20 °C/min in N_2, from room temperature to 600 °C. Limiting oxygen index (LOI) values were determined using an HC-2 oxygen index instrument according to ASTM D2863-00, with sample sheet dimensions of $150 \times 6 \times 3$ mm^3. Microscale combustibility tests were carried out on a Govmak MCC-2 microscale combustion calorimeter (USA). A sample of 3 to 5 mg was first kept at 100 °C for 5 min to remove the adsorbed moisture and then heated to 650 °C at a heating rate of 1 °C·sec^{-1} in a stream of nitrogen flowing at 80 cm^3·min^{-1}. The volatile thermal degradation products in the nitrogen gas stream were mixed with a 20 cm^3·min^{-1} stream of pure oxygen prior to entering a 1000 °C combustion furnace, and the heats of combustion for the pyrolysis products were measured using the oxygen consumption principle.

Scanning electron microscopy (SEM) of the char residues was done with an S-4800 microscope under an accelerating voltage of 3 kV. The char residues were obtained from the samples that were placed in a muffle furnace at 440 °C for 5 min.

RESULTS AND DISCUSSION

Synthesis and Characterization of PMPM

Synthesis of PMPM

The results of previous research (Moore and Tannahill 2001) indicated that DPA has two phenolic hydroxyls and one more active carboxyl. To avoid side reactions

(Moore and Tannahill 2001), the carboxyl group of diphenolic acid was protected prior to the polymerization process. By esterification of the carboxyl group with methanol, a linear polymer would be formed. On the other hand, the amidation of an ester is easier in comparison with the amidation of a carboxyl group.

Characterization of PMPM

The solubility of the products in selected solvents was measured qualitatively in this work. All polymers were insoluble in polar aprotic solvents (such as NMP, DMAc, and DMF), and only partially dissolvable in pyridine at room temperature, which exhibited their good solvent-resistance.

The chemical structure of PMPM-1 was confirmed by solid-state ^{13}C NMR and FTIR. A solid-state carbon nuclear magnetic resonance (^{13}C NMR) spectrum is shown in Fig. 1. Observed shifts, indicating the structure, were as follows for PMPM (75 MHz, ppm): 191~170(C=O), 156~140(=C-N, =C-O), 136~114(-ph), 53~41(CR_4), 33~22($-CH_3$, $-CH_2$).

The FT-IR spectra (KBr pellet) of PMP and PMPM-1 are shown in Fig. 2. The characteristic infrared absorbed peaks for PMP are at 2969 cm^{-1} ($C-H_3$), 1203 cm^{-1} (P=O), and 1078 cm^{-1} (P-O-C). It should be noted that after reacting with MA, the wave number of the $C-H_3$ groups shifts from 2969 cm^{-1} to 2975 cm^{-1}, and the peaks of the N-H groups and the C-N groups appear at 3409 cm^{-1} and 1647 cm^{-1}, respectively. That could demonstrate that MA has successfully reacted with PMP, catalyzed by zinc acetate.

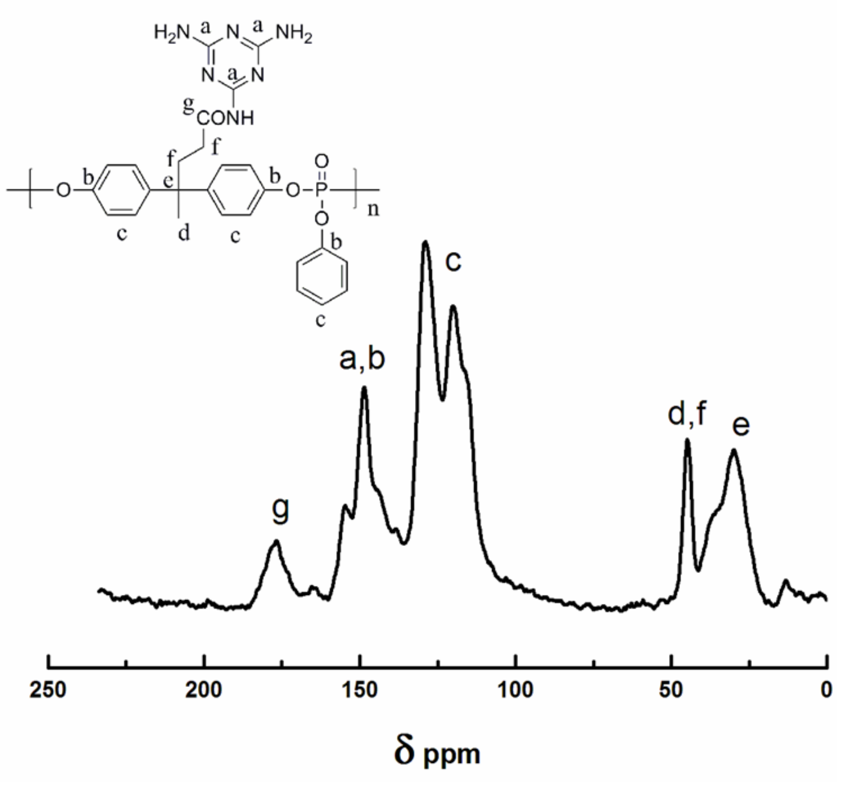


Fig. 1. Solid-state ^{13}C-NMR spectrum of PMPM-1

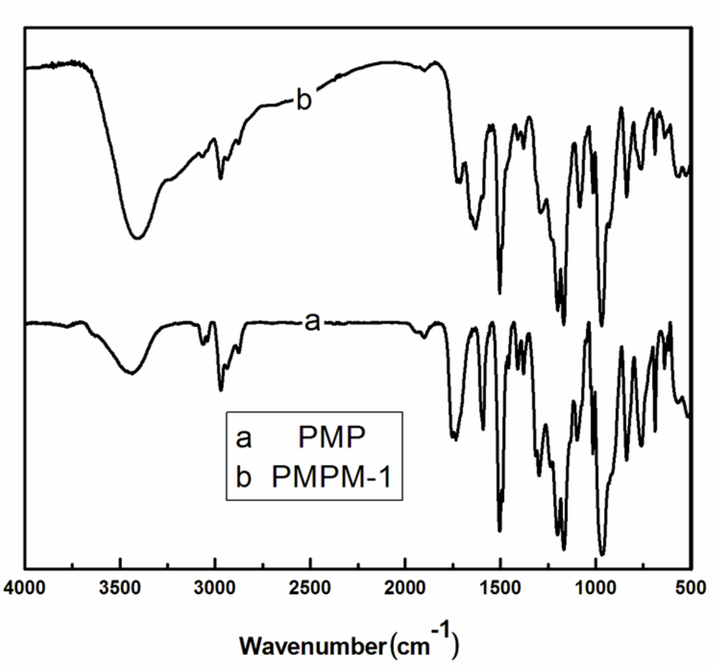


Fig. 2. FTIR spectra of PMP and PMPM-1

Thermal Properties of PMPM

To compare the differences in thermal stability of PDP (Chen *et al.* 2011), PMP, and PMPMs, the thermogravimetric (TG) and differential thermogravimetric (DTG) curves in N_2 for these compounds are presented in Fig. 3. The detailed thermal degradation parameters are summarized in Table 2. From the data in Table 2, it is apparent that the thermal stability of PDP (T_{onset} = 237 °C, T_{max1} = 254 °C) is not good enough to bear the processing temperature of ABS. The low thermal stability of PDP may contribute to the presence of carboxyl groups that started to decompose at about ~200 to 280 °C. As shown in Fig. 4, anhydride product formed by the condensation of carboxyl groups of PDP undergo further decarboxylation, resulting in increased crosslinking with increasing temperature, which tends to form a carbonaceous char. Such crosslinking is the primary reason for its good char-forming property.

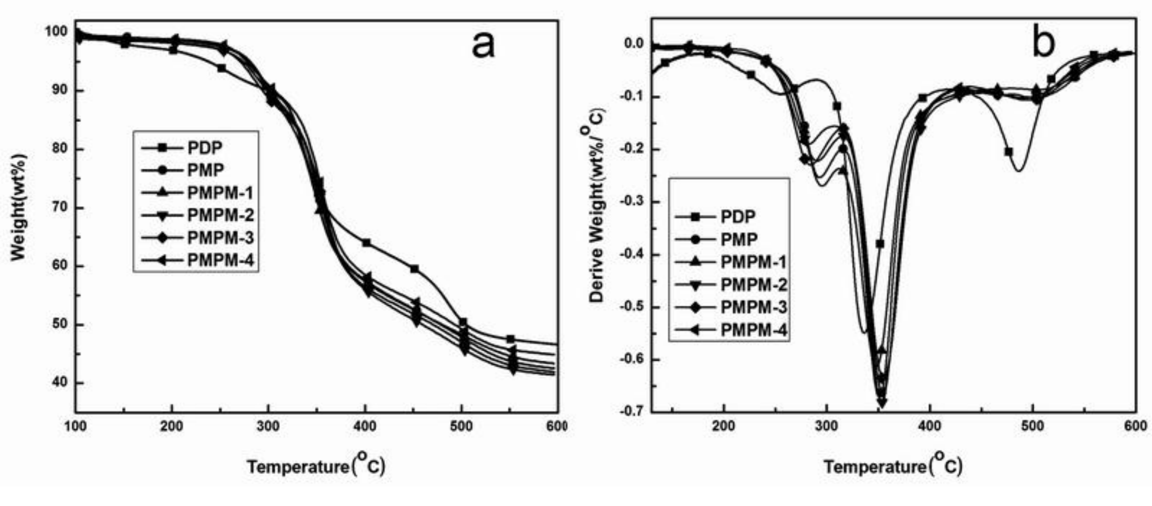


Fig. 3. TG(a) and DTG(b) curves of PDP, PMP, and PMPM flame retardants in N_2

With the protection of methyl esterification, the condensation of carboxyl groups was eliminated. Consequently, the thermal stability of PMP (T_{onset} = 283 °C, T_{max1} = 286 °C) is about 46 °C higher for T_{onset} and 32 °C higher for T_{max} than that of PDP. After the protection of methyl esterification, the decomposition of such molecules is changed to the cleavage of ester bonds, as shown in Fig. 4, which is more thermally stable than carboxyl groups. After the release of the small molecules such as NH_3, H_2O, and CH_3OH, such species can contribute to the formation of a crosslinked structure.

Two-step degradation was observed for all PMPMs at about 280 to 300 °C and 346 to 356 °C. According to Fig. 4, the first degradation could possibly be attributed to the degradation of amido bonds, while the second was responsible for the formation of residue char. Compared to PMP, PMPM-1 with amide started degrading at 287 °C and had a maximum decomposition temperature at 300 °C, which is about 4 °C and 14 °C higher than PMP, respectively. This is due to the fact that the amido bonds in samples PMPM were more stable than the methyl ester bond, which decomposed at a higher temperature. However, the thermal stability of the flame retardants (PMPM-1 to PMPM-4) decreased with the increase in nitrogen content. This is due to the fact that the sample with higher nitrogen content will release too much nitrogen gas, which may break the layered char. Without the protection of the layered char, the hot atmosphere can reach the underlying materials directly, and the polymer will decompose at a lower temperature (Qian *et al.* 2011).

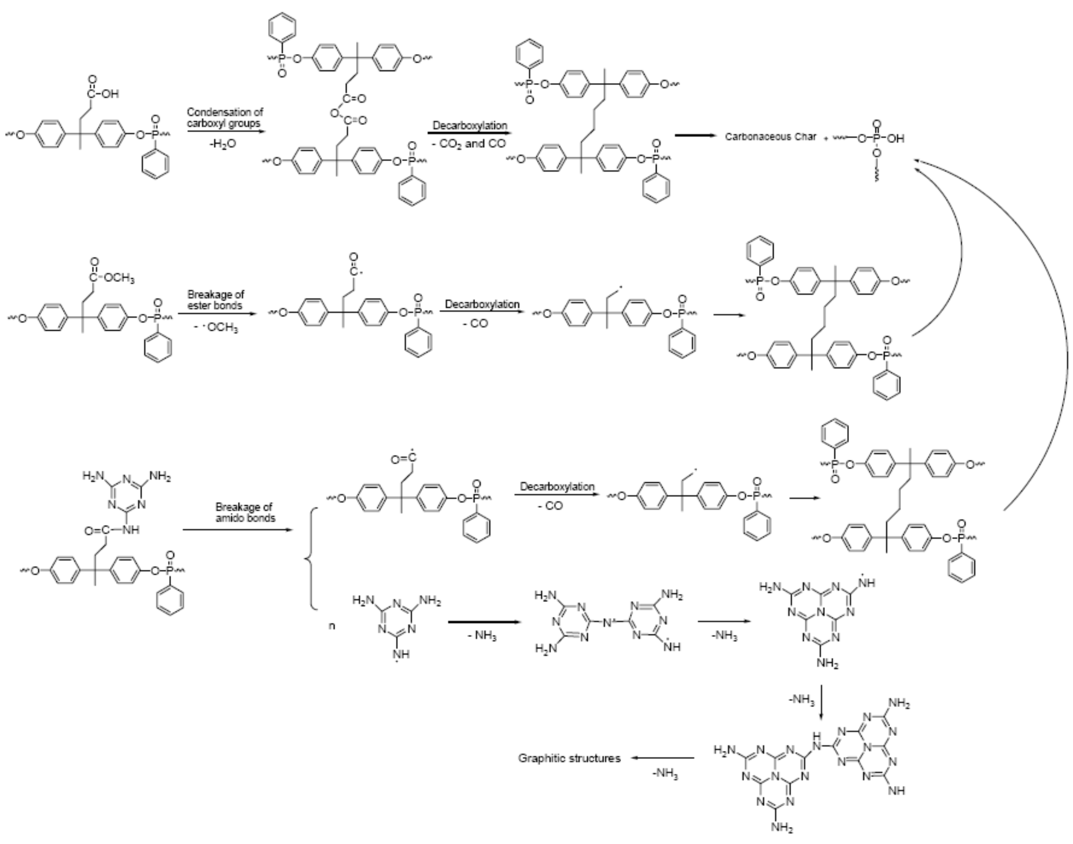


Fig. 4. The decomposition mechanisms of PDP, PMP, and PMPM

Table 2. Results of TG and DTG Analysis for Flame Retardants PDP, PMP, and PMPM in N_2 at a Heating Rate of 20 °C /min

Sample	$^{a}T_{onset}$ (°C)	$^{b}T_{max1}$ (°C)	T_{max2} (°C)	T_{max3} (°C)	Residue at 600 °C
PDP	237	254	335	486	46%
PMP	283	286	346	-	42%
PMPM-1	287	300	348	-	43%
PMPM-2	278	296	348	-	43%
PMPM-3	271	291	353	-	41%
PMPM-4	270	283	356	-	42%

$^{a}T_{onset}$: the onset point at 5 wt% weight loss; $^{b}T_{max}$: maximum decomposition temperature

Properties of the ABS/PMPM Blends

Thermal stability

The thermal degradation behaviors of ABS, ABS/PMP, and ABS/PMPM blends were investigated by TG analysis under a nitrogen atmosphere. The TG and DTG curves are given in Fig. 5. The detailed thermal degradation parameters are summarized in Table 3.

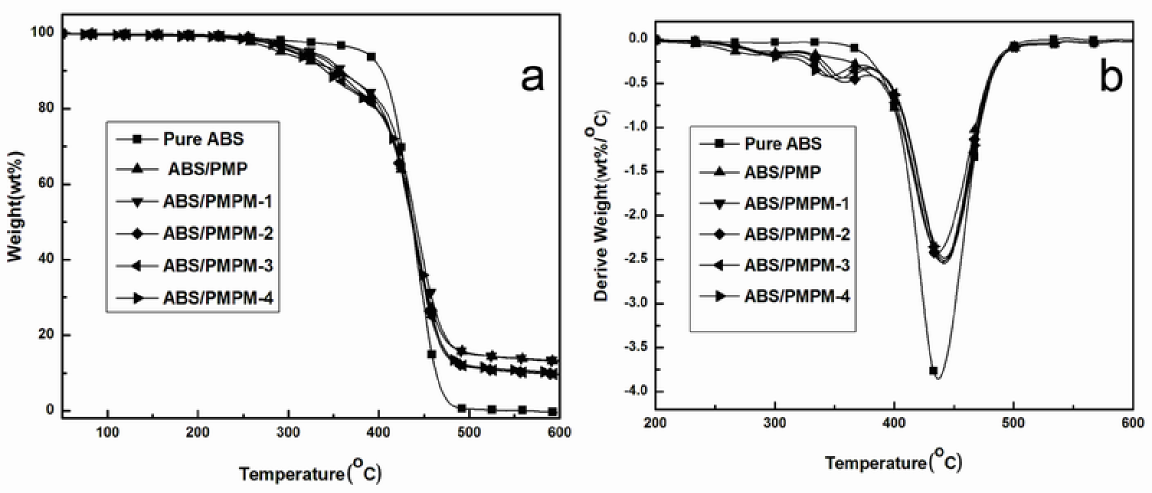


Fig. 5. TG (a) and DTG (b) curves of ABS blends in N_2

Table 3. Results of TG and DTG Analysis for ABS, ABS/PMP, and ABS/PMPM Blends in N_2 at a Heating Rate of 20 °C /min

Sample	T_{onset} (°C)	T_{max1} (°C)	T_{max2} (°C)	Residue at 600 °C
Pure ABS	383	-	431	0%
ABS/PMP	291	-	436	13%
ABS/PMPM-1	324	359	442	13.2%
ABS/PMPM-2	317	358	440	9.7%
ABS/PMPM-3	308	352	441	9.6%
ABS/PMPM-4	304	345	441	10.3%

As for pure ABS, its degradation started at 383 °C in N_2, and the maximum weight loss rate occurred at 431 °C without any char residue. The incorporation of PMP and PMPM flame retardants in ABS reduced the T_{onset}. However, $T_{\max}$ for ABS/PMP blend increased by 5 °C and ABS/PMPM systems increased by 9 to 11°C, indicating the enhanced thermal stability of ABS. According to Fig. 4, although the temperatures of the cleavage of the ester bonds and amido bonds are lower than that of ABS, such cleavage favors the formation of poly(phosphoric acid)s, which can accelerate the esterification and catalyze the cleavage of acetoxy groups to form more stable polynuclear aromatic structures (Xing *et al.* 2011; Ma *et al.* 2007; Song *et al.* 2009). Data from Table 3 shows that the T_{onset} of ABS/PMP is lower than that of ABS/PMPM-1~PMPM-4 because of the unstable thermal stability of methyl ester in PMP. As expected, the T_{onset} temperature of ABS/PMPM decreases along with the increase of nitrogen content in PMPM. The above results are in accordance with the TGA results of PMPMs. Compared with ABS/PMP, the T_{max}s of ABS/PMPM-1 to ABS/PMPM-4 improved by 4 to 6 °C. Due to the presence of melamine in PMPM-1 to PMPM-4, more residue char could be formed to improve the thermal stability of ABS at high temperature. It seemed that the higher the nitrogen content of PMPM, the lower the char residue. The results could be also attributed to the fact that the higher nitrogen content in flame retardants, the more gas such as ammonia is released during burning, so less char remains. According to the TGA result, ABS/PMPM-1 has the highest T_{onset}, T_{max}, and char residue of 324 °C, 442 °C, and 13.2%, respectively, which indicated that ABS/PMPM-1 is the best flame-retardant system in this work.

Flammability

LOI values for ABS, ABS/PDP, ABS/PMP, and ABS/PMPM, containing various nitrogen contents in PMPM are shown in Table 4. The LOI value for pure ABS is 17.8, indicating its flammability. As for the ABS/30% PMP system, the LOI value increased to 19.0, which is also higher than 18.6 for the ABS/30% PDP system (Chen *et al.* 2011), indicating PMPMs are more effective flame retardants than PDPs. The LOI values of ABS/PMPM blends all equaled 19.3, which represents an increase of 8.4% as compared with ABS. However, there were no obvious differences between the LOI values of different ABS/PMPM flame retardant systems. This may be attributed to the fact that the disparity in nitrogen content between PMPM flame retardants is not conspicuous enough for any difference to be reflected in LOI values.

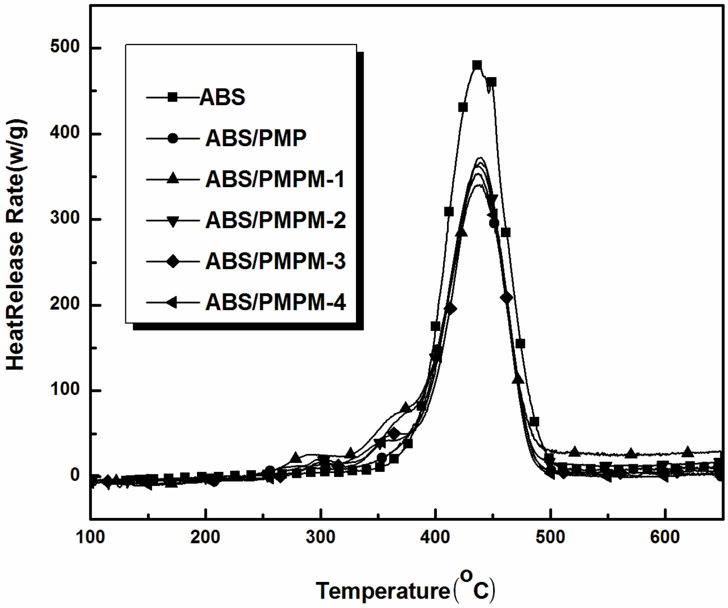


Fig. 6. HRR curves of ABS, ABS/PMP, and ABS/PMPM blends at 1 K/s heating rate

Table 4. LOI Values and MCC Data for ABS, ABS/PMP and ABS/PMPM Blends

Sample	[a]PHRR(w/g)	[a]THR(kJ/g)	[a]TEMP(°C)	[a]HRC(J/g-k)	LOI
Pure ABS	477.9	31.3	437.1	477	17.8
ABS/PMP	355	25.1	438	355	19.0
ABS/PMPM-1	342.9	23.5	440.5	345	19.3
ABS/PMPM-2	356.9	23.8	439.7	360	19.3
ABS/PMPM-3	370.4	24.1	439	374	19.3
ABS/PMPM-4	362.6	24.3	438	366	19.3

[a]PHRR: peak heat release rate; THR: Total heat release; TMEP: Temperature to PHRR; HRC: heat release capacity

For MCC measurement, only 5 to 10 mg samples were needed. Similar to the cone calorimeter, by this approach one can obtain the key fire parameters, including temperature at maximum heat release rate (T_p), the total heat release (THR in kJ·g^{-1}), peak heat release rate (PHRR in W·g^{-1}), and heat release capacity (HRC). From Fig. 6 and Table 4, it can be seen that the PHRR value of pure ABS was up to 478 kW/m^2, whereas it was reduced to 355 kW/m^2 in ABS/PMP blend and 342.9 to 370.4 kW/m^2 in the presence of PMPM in ABS. THR of ABS blends decreased from 31.3 to 23.5-25.1 kJ/g, with about 23% reduction. On the other hand, HRC decreased from 477 J/g-k to 345-374 J/g-k, with about 26% reduction, indicating the weakened flammability of ABS. Among the results of MCC, ABS/PMPM-1 also presented the lowest PHRR, THR, and HRC, which is in accordance with the TGA and LOI results.

Analysis of the residual chars

Figure 7 shows the SEM micrograph of the char residue from combustion of ABS/PMPM coating at 440 °C in a muffle furnace for 5 min. The char from ABS/PMPM-1 is shown as an intact, smooth, and compact structure, which was responsible for the flame retardancy of PMPM. The compact char layer could reduce both mass and heat transfer, prohibit the release of flammable gas from the inside, and also retard the degradation of the underlying materials.

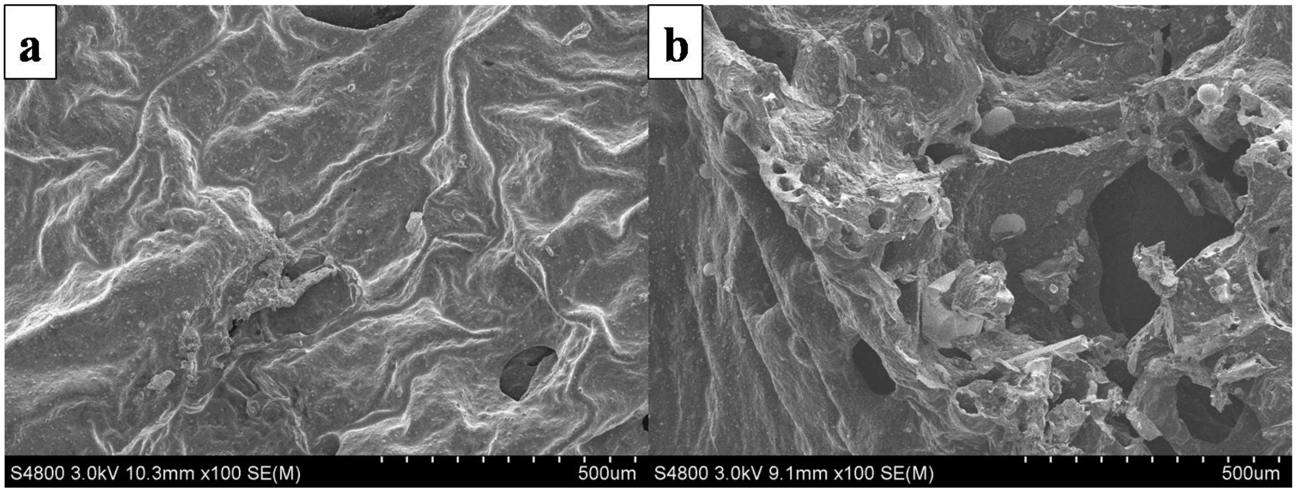


Fig. 7. SEM images of the outer surface of the char (×500): (a) ABS/PMPM-1; (b) ABS/PMPM-4

CONCLUSIONS

The production of chemicals from biomass represents a major challenge because of the complex nature of the biomass substrate. A series of novel oligomeric flame retardant PMPMs, using bisphenolic acid as raw material, were designed and synthesized in this work. Thermal stability and flame retardancy of ABS were enhanced with the incorporation of different PMPM samples containing different nitrogen contents, as evidenced by TGA, LOI, and MCC analyses. The results showed that after esterification and amination of carboxyls, PMPM samples have higher thermal stability and flame retardant efficiency. Among the PMPMs, PMPM-1 flame retardants having an elemental nitrogen content of about 1.8 wt% resulted in higher char yield with an intact, smooth, and compact structure, which was responsible for the enhanced thermal stability and improved flame retardancy performance of ABS. Due to the scarcity of nonrenewable petroleum as a resource, raw material was replaced in part by chemicals derived from biomass, and this can be a potential approach for the sustainable development of IFRs. Further research and development is required to increase the flame retardant efficiency for flame retardants derived from biomass.

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